Preparation of Acrylic and Methacrylic Acids by Pyrolysis of Their Alkyl Esters

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The purpose of this investigation was to effect the synthesis of acrylic and methacrylic acids by thermal decomposition of their ethyl or higher alkyl esters. The analogous pyrolysis of ethyl crotonate into crotonic acid is known[2] to occur. Since it appeared that such a synthesis might be more practical than the alternative approach by hydrolysis[3,4,5,6] the present investigation was undertaken.

In this investigation it has now been found (Table I) that both acrylic acid and methacrylic acid can be prepared conveniently and in high yields by passing suitable acrylic or methacrylic esters through a Pyrex glass tube heated at about 500 to 580°. The acids produced in this manner are relatively pure, contain little or no water, and are readily purified by distillation or crystallization.

As would be expected from previous observations[7] made with acetates of secondary alcohols, *s*-butyl acrylate decomposed more readily than did the esters of primary alcohols. Isobutyl acrylate was more stable than the other esters studied. Possibly this stability is attributable to the presence of only one hydrogen on the β-carbon atom of the alkyl group. Ethyl acrylate, ethyl methacrylate, and *n*-butyl methacrylate appeared to have approximately the same thermal stability. Cyanoethyl acrylate was much less stable than ethyl acrylate.

Contact time was relatively unimportant at 570 to 580°, 90 to 94% of the ethyl acrylate being decomposed when the contact time was four to twelve seconds. At lower temperatures, however, the influence of contact time was more marked. Considerable quantities of acrylic acid have been prepared conveniently in this Laboratory by pyrolyzing ethyl acrylate under conditions similar to those of Experiment 3, Table I.

The high yields of acrylic and methacrylic acids and the relative unimportance of contact time at the higher temperatures show that these acids are relatively thermostable. That methyl acrylate is rather stable is demonstrated by its preparation in high yield by the thermal decomposition of the acetyl derivative of methyl lactate.[8] The fact that acrylic acid was not obtained in the pyrolysis[8] of ethyl acetoxypropionate indicates that α-acetoxypropionic acid instead of ethyl acrylate was the principal primary decomposition product.

Table I

Pyrolysis of Alkyl Acrylates and Methacrylates

Expt.	Grams pyrolyzed	Addition rate, moles of ester per hr.	Temp., °C.	Contact time, sec.	Ester decomposed, %	Gases and losses, %	Yield of unsaturated acid, %[a]
			Ethyl Acrylate				
1	161.2	0.84	499	6.9	39.7[b]	13.7	81[c]
2	203.7	0.57	556	10.7	92.8[b]	28.2	94[c]
3	175.8	1.17	568	4.5	89.8[b]	27.4	90[c]
4	677.2	1.38	574	3.9	90.9[d]	28.7	92[d]
			Isobutyl Acrylate				
5	76.3	0.83	545	7.3	84.5[e]	36.8	63[e]
			s-Butyl Acrylate				
6	140	.77	498	8.4	100[b]	40.2	97[c]
			β-Cyanoethyl Acrylate				
7	98.7	.74	500	7.9	about 92[f]	17.7	74[c,g]
			Ethyl Methacrylate				
8	149.3	.76	497	7.6	44.1[d]	11.5	79[d]
9	150.0	.99	550	5.5	83.7[b]	26.2	82[d]
10	156.1	.74	579	7.1	100[d]	30.6	87[d]
			n-Butyl Methacrylate				
11	150.1	.49	513	11.6	79.2[d]	17.7	78[d]
12	149.2	.55	555	9.7	96.8[d]	34.7	93[d]
13	151.6	.55	586	9.5	98.0[d]	37.4	91[d]

[a] Yield (per cent. of theoretical) based on unrecovered ester. [b] From distillation data. [c] From titration and distillation data; the yield based on unsaturated acid actually isolated by distillation was usually lower. [d] From titration and saponification data. [e] From titration and saponification of the distilled pyrolysis products; separation by distillation was difficult. [f] About 8% of the products appeared as distillation residue, possibly polymeric material. [g] The yield of acrylonitrile, determined by distillation, was 86.5%.

In a single experiment on the pyrolysis of *n*-butyl crotonate at 537° and 7.2 seconds, 88% of the ester was cracked. The yields of crotonic acid and butylene were 84 and 85%, respectively.

Acrylic acid was made also by the acidolysis of methyl acrylate with formic or acetic acid in the presence of a small amount of sulfuric acid and hydroquinone. Formic acid was preferable because it reacted much more rapidly than acetic acid. The highest yield of acrylic acid (80%) was

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) N. T. M. Wilsmore and A. W. Stewart, *Proc. Chem. Soc.*, **23**, 309 (1908); C. D. Hurd, "The Pyrolysis of Organic Compounds," Reinhold Publishing Corp., New York, N. Y., 1929, 807 pp.

(3) D. Pressman and H. J. Lucas, This Journal, **64**, 1953 (1942).

(4) C. F. Koelsch, *ibid.*, **65**, 437 (1943).

(5) O. C. Dermer, W. G. Markham and H. M. Trimble, *ibid.*, **63**, 3524 (1941).

(6) H. T. Neher, *Ind. Eng. Chem.*, **28**, 267 (1936).

(7) A. J. Van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

(8) R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935).

obtained when the acidolysis was carried out with formic acid. The acidolysis method of preparing acrylic acid is similar to the pyrolysis method in that water is not a reactant or product.

Experimental

Acrylic Esters.—Commercial samples of ethyl acrylate, ethyl methacrylate, and *n*-butyl methacrylate were used without purification or the removal of inhibitor. The isobutyl, *s*-butyl, and cyanoethyl esters of acrylic acid were prepared by the alcoholysis of methyl acrylate.[9]

Pyrolysis Experiments.—The equipment and general procedure were essentially similar to those previously described.[10] The esters, which contained a small proportion of hydroquinone, were pumped into the top of the vertical Pyrex glass tube with a constant-feed pump of the type described by Corson and Cerveny.[11] The heated portion of the pyrolysis tube was packed with short lengths of Pyrex glass tubing. A small quantity of hydroquinone was placed in the cooled receiver of the pyrolysis unit to inhibit polymerization. Small amounts of water, which distilled azeotropically with ethyl acrylate, were present in the products formed under the more drastic conditions.

Use of a vaporizer to introduce the esters as vapor into the pyrolysis tube seemed beneficial. In an early experiment, for example, a vaporizer was not employed, and the pyrolysis products were brown. In the succeeding experiments a vaporizer was used, and under otherwise similar conditions the products were amber or light yellow.

The yield of acrylonitrile in Experiment 7 was 86.5%. The yields of olefins were sometimes ignored, but the yields of normally gaseous material collected in solid carbon dioxide traps (assumed to be butene) were 83 and 86% in Experiments 12 and 13, respectively.

Isolation of Acrylic Acid from the Pyrolysis Products.—The separation of acrylic acid and isobutyl acrylate by distillation was difficult because of the proximity of their boiling points. The principal difficulty experienced in fractionally distilling the other pyrolysis products arose from the tendency of acrylic acid and its esters to polymerize. For the purpose of preventing or minimizing polymerization, the distillations were carried out below 100-mm. pressure (preferably at about 20 mm.); hydroquinone was always placed in the distilling flask; and carbon dioxide instead of air was led into the distilling flask to prevent bumping. A distilling column filled with copper rings of the Fenske[12] type was used in some of the distillations. The influence of pressure upon the boiling points of acrylic and methacrylic acids is indicated in Figure 1.

The likelihood of polymerization is less when acrylic and methacrylic acids are purified by crystallization (acrylic acid and methacrylic acid melt at approximately 14 and 15°, respectively). In some instances the pyrolysis products were cooled to cause crystallization; the mixture was decanted, and the solid material was allowed to melt. The products of Experiment 4, Table I, were purified by freezing and decanting (three times) and by distillation. The composition of the pyrolysis product as indicated by these methods is given in Table II.

By freezing and decanting, methacrylic acid having a purity of 98.7% (determined by titration) was obtained from some pyrolysis products.[13]

Acrylic Acid by Acidolysis of Methyl Acrylate.—Four moles (184 g.) of formic acid, 12 moles (1032 g.) of methyl acrylate, 30 g. of hydroquinone and 2 cc. of sulfuric acid were mixed and refluxed in a still having a 3-foot column and a variable take-off head. The still was operated with total reflux until the temperature at the head fell to 32°. Methyl formate was withdrawn, as formed, for eight to twelve hours, when its production ceased. The excess methyl acrylate was then distilled at a pressure of 140 mm., after which acrylic acid of a high degree of purity was distilled at 56° (25 mm.). The yield was 231 g. (80% of the theoretical, based on the formic acid). Over 91% of the methyl acrylate put into the reaction mixture was either recovered or converted into acrylic acid. The acrylic acid (to which had been added 10 g. of hydroquinone) was redistilled and the following constants were determined: b. p., 71° (50 mm.); n^{20}_{D}, 1.4210; d^{20}_{4}, 1.0487; *MR*, calcd., 17.12; found, 17.43 (the calculated value contains no increment for the conjugation)

A similar acidolysis experiment, using acetic instead of formic acid, was much less satisfactory. The rate of reaction was much lower, and the conversion was far from complete even after several days of refluxing. Also, the distillation of the reaction mixture was complicated by the necessity of separating methyl acetate, methyl acrylate, acetic acid, and acrylic acid.

TABLE II

ANALYSIS OF PRODUCTS OF EXPERIMENT 4

Method of analysis or separation	Ethyl acrylate, % Recovered	Converted into acrylic acid	% Acrylic acid yield	Purity[a]
Freezing and decanting[b]	9.2	67.1	74.0	96.4
Distillation	8.6	82.8	90.6	97.5
Titration and saponification	9.1	84.2	92.4	..

[a] Content of acrylic acid was determined by titration.
[b] Acrylic acid purified in this manner was light amber.

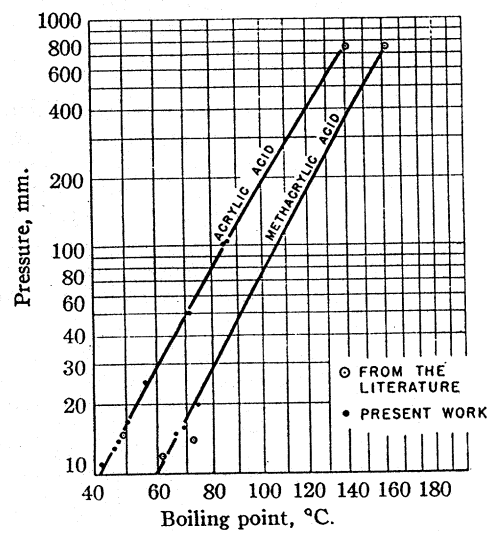

Fig. 1.—Boiling points of acrylic and methacrylic acids at different pressures.

Summary

The principal products obtained in the thermal decomposition of several alkyl acrylates and methacrylates were acrylic or methacrylic acid and olefins corresponding to the alkyl group. Alkyl acrylates were increasingly stable in this order for

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(10) E. M. Filachione, J. H. Lengel and C. H. Fisher, *ibid.*, **66**, 494 (1944).

(11) B. B. Corson and W. J. Cerveny, *Ind. Eng. Chem., Anal. Ed.*, **14**, 899 (1942).

(12) M. R. Fenske, C. O. Tongberg and D. Quiggle, *Ind. Eng. Chem.*, **26**, 1169 (1934).

(13) In handling the products it is advisable for the operator to wear rubber gloves, since both acrylic and methacrylic acids have a delayed corrosive action on the skin.

alkyl groups: *s*-butyl < 2-cyanoethyl < ethyl and *n*-butyl < isobutyl. The pyrolysis of appropriate acrylic and methacrylic esters constitutes a convenient method for preparing the corresponding unsaturated acids.

The acidolysis of methyl acrylate with formic acid is described.